

ELECTROLYTIC PRODUCTION OF OXYGEN FROM LUNAR RESOURCES

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Abstract

Oxygen is a valuable commodity in space. Substantial savings have been projected for future missions if oxygen could be produced on the moon from local resources.

Some of the most promising approaches to extract oxygen from lunar resources involve electrochemical oxygen generation. In a straight-forward concept called "magma electrolysis", suitable oxides (silicates) are molten at 1300-1500 °C and the melt electrolyzed. Residual melt can be discarded after partial electrolysis. Alternatively, lunar soil may be dissolved in a molten salt and electrolyzed. In this approach, temperatures are lower and melt conductances higher, but electrolyte constituents need to be preserved. Both possibilities are being studied in the laboratory.

In a different approach, ilmenite is reduced by hydrogen and the resulting water electrolyzed (Carbotek Process TM).

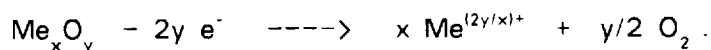
Although know-how from terrestrial technology can be applied, the process task is unconventional and requires many innovative solutions. Time and effort needed for successful development should not be underestimated.

Oxygen from Lunar Resources

Due to the effort necessary to transport it there from Earth, oxygen is a precious commodity in space. Oxygen is needed for life support and, in larger amounts, also for propulsion. In situ preparation of oxygen from local resources in space can reduce costs for future missions in space. The lunar surface is an appropriate site to establish an oxygen manufacturing capability.

Molecular oxygen may be prepared from oxides by electrolysis. In the absence of volatile oxides, solid oxides may be used. Such oxides are readily available on the lunar surface, mainly as silicates of various compositions. Lunar soil may be regarded as an already adequately comminuted raw material. Highland soils are anorthositic, feldspar-like, with compositions similar to the one given as an example in Table 1. Soils of the mare region have a more basaltic character and are represented in Table 1 by a composition indicated by Washington University authors [1] as representative.

In the electrolytic decomposition of the oxides, oxygen gas is produced at the positive electrode, the anode. The reaction may be formulated as follows:



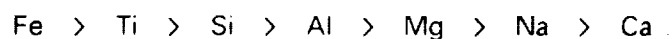
Metallic components, meanwhile, are reduced at the cathode:

Table 1. Compositions of Lunar Soils

	<u>Anorthositic Soil [2]</u>	<u>Basaltic Soil [1]</u>
SiO ₂	44.9 wt%	46.2 wt%
Al ₂ O ₃	27.6 wt%	12.6 wt%
FeO	5.03 wt%	17.4 wt%
TiO ₂	0.55 wt%	2.8 wt%
MgO	5.35 wt%	10.4 wt%
CaO	15.8 wt%	10.5 wt%
Na ₂ O	0.39 wt%	
K ₂ O	0.10 wt%	



Various metals are reduced with different ease. Theoretical decomposition potentials for the oxides can be calculated from thermodynamic data, but they are modified as the oxides combine to mixed oxide compounds. For the major components of the oxides discussed, the following order of decreasing (more negative) cathodic deposition potential appears to exist:



The cathodic products may be of no substantial interest and may even be discarded. Silicon and aluminum, on the other hand, may be the products of major interest. Depending on the desirability to produce and collect the metals, the process may be refined to various degree [3], as illustrated by Figure 1.

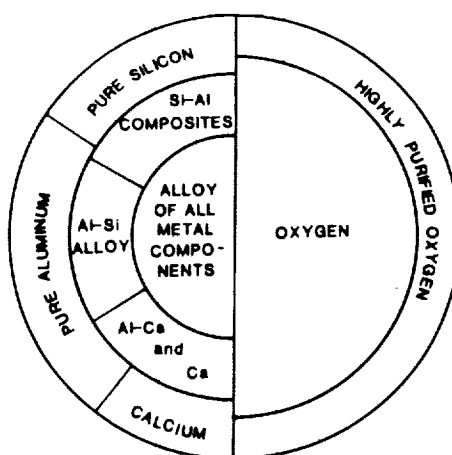


Figure 1. Refinement of Lunar Molten Salt Electrolysis Depending on Metallic Products Desired

Two major approaches to the electrolysis of lunar oxides are being explored: (1) a molten silicate electrolysis in which the oxides are melted and the melt electrolyzed, and (2) a fused salt electrolysis in which the oxides are dissolved in a molten salt (flux) and electrolyzed.

Electrolysis of Molten Silicates

Lunar raw material may be molten and electrolyzed at temperatures of 1400 – 1500 °C. This can be accomplished in a batch mode, whereby the electrolyte composition changes during the course of electrolysis; at a certain point, the residual melt is discarded. Such an approach was discussed in an earlier publication by Washington University authors [1].

Alternatively, the electrolysis may be conducted in a quasi-continuous mode. Fresh ore is added to an electrolyte which represents partially electrolyzed raw material. While components that reduce most easily are continuously electrolyzed, electrolyte is gradually removed from the system. This approach is represented in Figure 2.

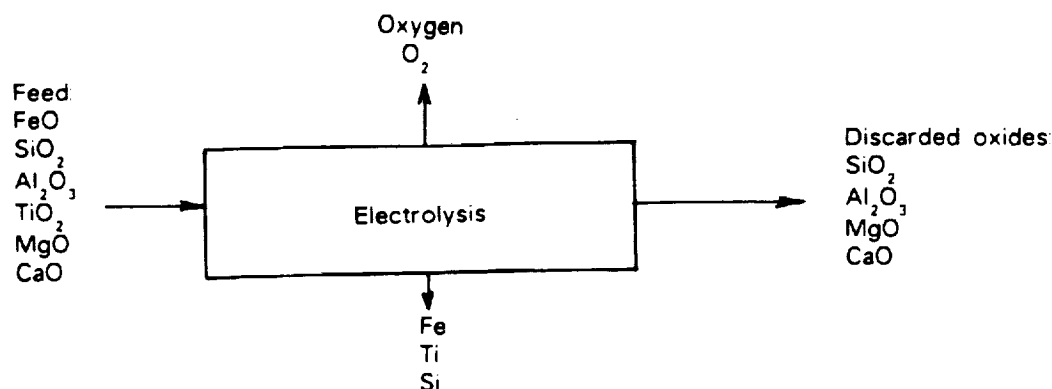


Figure 2. Continuous Electrolysis of Molten Oxides

A cell design for such an electrolysis, with a molten silicon-iron cathode, has been suggested by McCullough and Mariz [4].

Electrolyte conductivities vary significantly with composition. Haskin et al [1] give the following regression equation (for 1425 °C):

$$\ln \lambda = 5.738 - 12.6[\text{SiO}_2] - 10.0[\text{AlO}_{1.5}] - 3.7[\text{TiO}_2] + 1.89[\text{FeO}] + 0.07[\text{MgO}] - 1.25[\text{CaO}]$$

(λ in $\text{ohm}^{-1}\text{cm}^{-1}$; symbols for oxides stand for mole fractions).

High iron oxide contents obviously lead to relatively high conductances. Excessive silicon contents result in low conductivities. In practice, one may expect to be operating with electrolytes of specific conductivities of about $0.3 \text{ ohm}^{-1}\text{cm}^{-1}$.

So-called "magma electrolysis" experiments have been conducted by L. A. Haskin and his co-

workers at Washington University. They gathered essential basic data on the electrolyte properties and electrolyzed small molten charges suspended in platinum wire loops. Recently, experiments were conducted in small spinel crucibles. EMEC Consultants started investigations using alumina crucibles, a platinum anode and a graphite cathode. Cathodic deposits will be examined and several anode candidates and other materials tested in future work.

Electrolysis in Molten Salt

Lunar soil may be dissolved in a suitable electrolyte of molten fluorides and electrolyzed at temperatures of about 1000 °C. It is important that all components added to the electrolyte are removed again from the system. In the approach envisioned by EMEC Consultants, this is accomplished by complete electrolysis (separation of some components as undecomposed oxides would also be possible). Electrolysis conditions are such that the component most difficult to decompose reacts. As this component is calcium, a cathode potential, therefore, is maintained which permits reduction of calcium; the other metals are co-reduced at the rate they reach the cathode, i.e. at the mass transport limited rate. This approach has, thus, been called a "calcium-plus electrolysis".

Calcium fluoride, with a very high theoretical decomposition voltage, would be a desirable electrolyte, but its melting point is high. Also metal solubilities leading to current efficiency losses would be excessive. A mixture of calcium fluoride and lithium fluoride is preferable as electrolyte, as added lithium fluoride reduces operating temperatures. The presence of lithium fluoride, however, leads to a cathodic co-deposition of lithium which has to be recovered in an auxiliary metal separation step, presumably by vacuum distillation.

Oxygen is evolved at the anode as a gas. Some electrolyte components will evaporate into this gas but may be retained by process feed through which the off-gases are bled, similar to the recovery of fluorine values in the fume treatment of commercial aluminum production. Traces of sulfur dioxide may remain with the oxygen and should not affect the performance of the oxygen as propellant. It may be possible to obtain oxygen feasible for life support by simple reevaporation of liquefied oxygen.

The envisioned molten salt electrolysis process to produce oxygen is summarized in Figure 3.

The development of this process actually started with work on a concept to produce silicon and aluminum from lunar resources [5]. In a stepwise reduction process, silicon of the anorthite feed is reduced chemically by aluminum metal. Aluminum oxide and calcium oxide are electrolyzed in a second major process step. Auxiliary process steps involve the beneficiation of lunar soil by magnetic separation to yield a good-quality anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) feed, the separation of silicon from a hypereutectic Si-Al alloy, the purification of oxygen by exposing the cell gases to feed ore, and the separation of lithium from the cathode metal.

Other Approaches

Ilmenite reduction with hydrogen is practiced in the Carbotek process [6]. This process includes an electrochemical step, as the water produced by the reaction of hydrogen with ferrous oxide is electrolyzed. An electrolysis at high temperatures is proposed but has not been explored in Carbotek's experimental work.

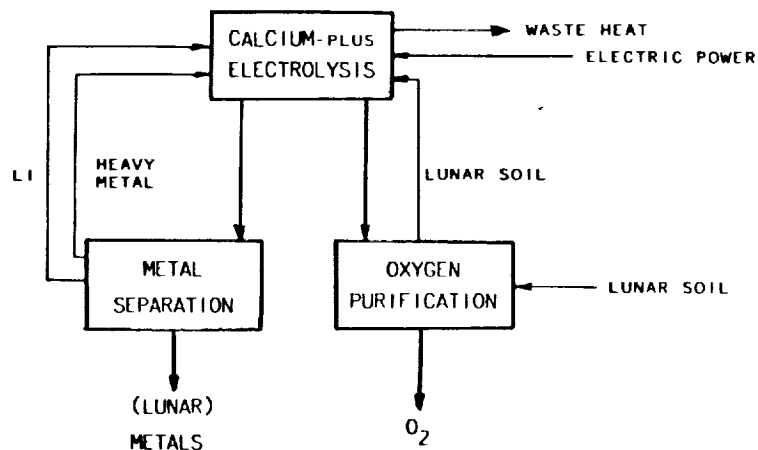


Figure 3. "Calcium-plus Electrolysis" to Produce Oxygen From Lunar Soil

Concluding Remarks

There does not appear to be a clearly favored process to produce lunar oxygen at this time. All approaches discussed above include unconventional process elements with various degree of uncertainty regarding their technical feasibility [7]. Additional research is required. Materials stability problems need to be addressed. In particular, a suitable anode for the evolution of oxygen needs to be identified. Such work is in progress at EMEC Consultants.

After investigating the chemistry of individual process steps, processes shall be demonstrated on the bench scale. It is estimated that 8 to 12 years of additional work will be required before a successful pilot demonstration may be undertaken [8]. Time periods for the development of new processes or process variants in terrestrial extractive metallurgy, which is directly related to the discussed approaches, are considerable. Time and effort necessary to develop a lunar oxygen extraction process should not be underestimated.

Acknowledgements

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References

- [1] L. A. Haskin, R. O. Colson, D. J. Lindstrom, R. H. Lewis, and K. W. Semkow .
Electrolytic Smelting of Lunar Rock for Oxygen, Iron, and Silicon .
Revised Manuscript , 1989 .
- [2] R. J. Williams and J. J. Jadwick, editors .
Handbook of Lunar Materials .
NASA Reference Publication 1057 , 1980 .
- [3] D. L. Anthony, C. N. Cochran, W. C. Cochran, W. E. Haupin, R. Keller, and K. T. Larimer .
Products from Lunar Anorthite .
Space Manufacturing 7; Proceedings of the Ninth Princeton/AIAA/SSI Conference :86-89
 , 1989 .
- [4] E. McCullough and C. Mariz .
Lunar Oxygen Production Via Magma Electrolysis .
In *Proceedings of Engineering, Construction and Operations in Space II, Space 90, Al-
buquerque NM* . April , 1990 .
- [5] D. L. Anthony, W. C. Cochran, W. E. Haupin, R. Keller, K. T. Larimer .
Dry Extraction of Silicon and Aluminum from Lunar Ores .
Lunar Bases & Space Activities in the 21st Century Paper No. LBS-88-066 : , 1988 .
- [6] M. A. Gibson and C. W. Knudsen .
Development of the Carbotek Process for Lunar Oxygen Production .
In *Proceedings of Engineering, Construction and Operations in Space II, Space 90, Al-
buquerque NM* . April , 1990 .
- [7] R. Keller .
Lunar Production of Aluminum, Silicon and Oxygen .
*Metallurgical Processes for the Year 2000 and Beyond, edited by H. Y. Sohn and
E. S. Geskin, published by The Minerals, Metals & Materials Society* :551-562 .
1989 .
- [8] EMEC Consultants
Production of Oxygen by Electrolysis of Lunar Soil in Molten Salt
NASA Phase II Proposal . 1990